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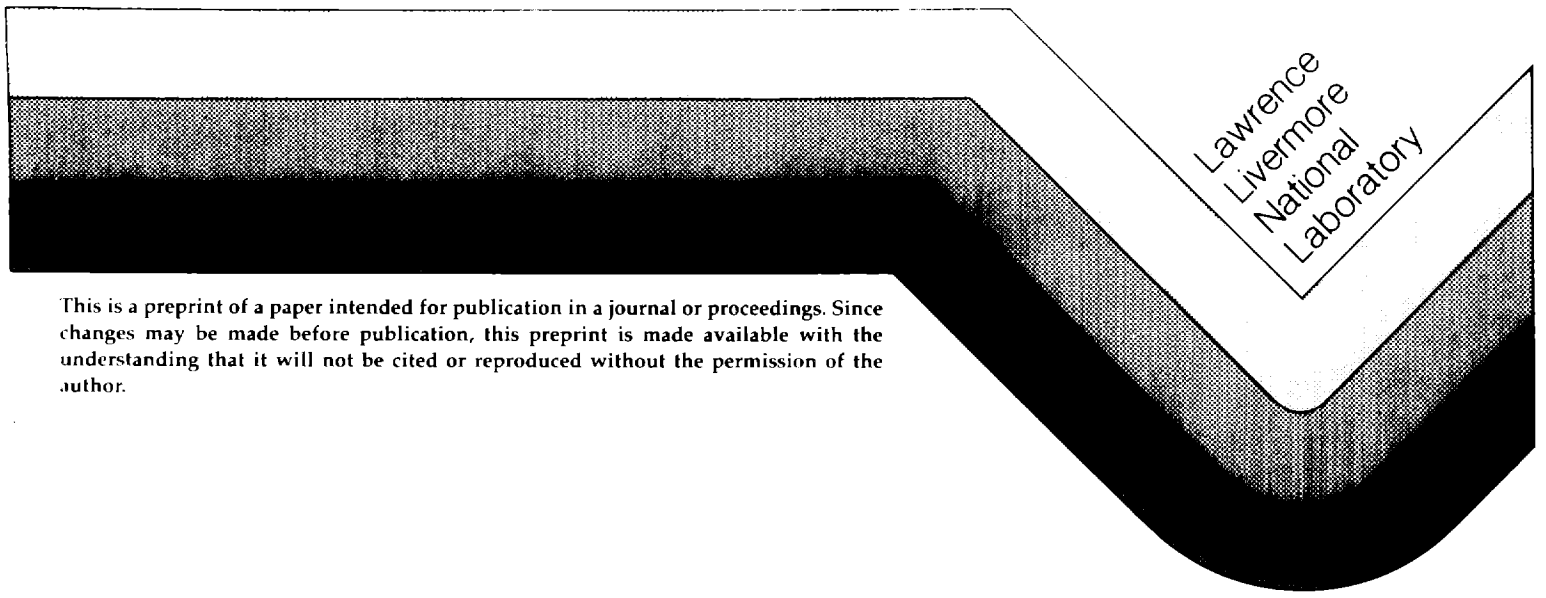

DEVELOPMENT OF ACCURATE ESTIMATION METHODS FOR CALCULATING HEAT CAPACITIES OF REFRACTORY MATERIALS*

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ABSTRACT

Factors that contribute to the heat capacities of solids are analyzed and correlation methods are developed for accurately estimating these factors for the refractory borides, carbides, nitrides, and oxides. High temperature heat capacities calculated for the borides are found to agree with experiment to within ±3%.

INTRODUCTION

Accurate heat capacity data are needed over the entire solid temperature range for refractory borides, carbides, nitrides, and oxides to develop a proper thermodynamic data base. Since it would be formidable to measure all the required heat capacities, accurate estimation methods are highly desirable. The approach used here for making accurate estimates is to analyze the various factors that comprise the overall heat capacity, and to apply correlation methods to estimate the parameters required by theory for evaluating the factors. It will be shown in the discussions that follow that the input parameters required are: thermal expansivity, Grüneisen gamma, Debye temperatures for metal and nonmetal atoms, electronic gamma, f electron energy states, spin-order magnetic states, and energies and entropies of formation of lattice defects.

The heat capacity at constant pressure, C_p, is the quantity ordinarily needed in thermodynamic calculations. C_p is related to C_v, the heat capacity at constant volume, by the relation

$$C_p = C_v + \frac{\beta^2 \bar{V} T}{\chi_T}, \qquad (1)$$

where β is the volume thermal expansivity, V is the molar volume, and χ_T is the isothermal compressibility. The quantity, $\beta^2 \bar{V} T/\chi_T$, is known as

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the dilatation term. C_v is made up of the following terms:

$$C_v = C_\ell + C_a + C_e + C_f + C_m + C_d, \tag{2}$$

where C_ℓ is the term for harmonic lattice vibrations and constitutes the main part of C_v, C_a is for anharmonic lattice vibrations, C_e for conduction electrons, C_f for f electron states, C_m for spin-order magnetic states, and C_d for lattice defects.

DILATATION TERM

Following the approach used by Hoffman and co-workers,[1] the dilatation term may be rewritten in terms of the Grüneisen constant, γ_G, as

$$\beta^2 \bar{V} T/\chi_T = \beta \gamma_G T C_\ell, \tag{3}$$

where γ_G is equal to $\beta\bar{V}/\chi_T C_\ell$. Evaluation of the dilatation term therefore depends upon values for β and γ_G. The dilatation term contributes to ∿1% to C_p at 300 K, increasing to ∿15% near the melting point.

To evaluate β, we can refer to available data,[2] or use a method developed by the author[3] using the relation

$$\beta = 21.1\ \Delta E_a^{-1}\ (T/h)^{1/3}, \tag{4}$$

where ΔE_a is the atomization energy in kJ/g-atom and h is the Knoop microhardness in HK units under ∿50 g load. The $T^{1/3}$ power temperature dependence for β given in equation (4) is a good approximation over the entire solid range, and even a rough estimate of h gives a good estimate of β, since the h values are raised to the -1/3 power.

To evaluate γ_G, a tabulation is made of the available room temperature data on β, $\bar{V}$, χ_T, and C_ℓ for several borides, carbides, nitrides, and oxides (see Table 1). Examination of the γ_G data shows that a definite trend exists in γ_G with class of substance. Studies made of the temperature dependence of γ_G from room temperature to ∿1300 K for borides[4] and oxides[5,6] indicate that γ_G remains constant with temperature. It seems reasonable to assign a constant γ_G value of 1.2 for the borides and carbides, and 1.4 for the nitrides and oxides.

HARMONIC LATTICE VIBRATIONS

Hoffman et al.[1] showed that the low temperature heat capacities of carbides, nitrides, oxides, and fluorides could be adequately described by Debye functions if two Debye temperatures were assigned to each compound: one for the metal (θ_R) and the other for the nonmetal (θ_X) constituent (see Table 2). They further showed that if all the atoms in a crystal have equal mean-square displacements, then θ_R and θ_X should be inversely proportional to the square roots of the respective masses, i.e.,

Table 1 Room temperature values of thermal expansivity, molar volume, compressibility, heat capacity, and Grüneisen gamma for a number of refractory substances.

Substance	β, K^{-1} X 10^{-5}	$\bar{V}$, cm^3/mole	χ_T, cm^2/dyne X 10^{-12}	C_ℓ, ergs/mole-K X 10^8	γ_G
TiB_2	1.6[2]	15.38[7]	0.47[4]	4.39[13]	1.2
ZrB_2	1.4[2]	18.53[7]	0.46[4]	4.82[13]	1.2
HfB_2	1.4[2]	17.87[7]	0.49[4]	5.02[13]	1.0
B_4C	1.1[2]	21.94[7]	0.39[9]	5.26[14]	1.2
TiC	1.6[2]	12.18[7]	0.48[7]	3.36[14]	1.2
ZrC	1.4[2]	15.50[7]	0.47[9]	3.79[14]	1.2
UC	2.3[2]	18.35[7]	0.61[10]	5.01[15]	1.4
TiN	1.8[2]	11.38[7]	0.34[7]	3.71[14]	1.6
UN	2.1[2]	17.60[7]	0.54[11]	4.78[16]	1.4
BeO	1.8[2]	8.32[8]	0.46[12]	2.54[14]	1.3
MgO	2.9[2]	11.25[8]	0.62[8]	3.78[14]	1.4
Al_2O_3	1.7[2]	25.57[8]	0.38[8]	7.90[14]	1.4
ThO_2	2.0[2]	26.38[8]	0.56[9]	6.10[14]	1.5
UO_2	2.3[2]	24.62[8]	0.62[9]	6.41[14]	1.4

$$\theta_R/\theta_X = (M_X/M_R)^{1/2}. \qquad (5)$$

θ_R/θ_X values were found to deviate by a factor of 2 from Equa. (5).

Kaufman[17] calculated θ_R and θ_X for several diborides (see Table 2) by imposing Equa. (5), along with a condition that the S°_{298} values calculated by Debye functions be made to agree with experimental S°_{298} values. A comparison of Kaufman's values with experimental C_p values shows that the equal mean-square displacement assumption fails for HfB_2 and is only roughly correct for other diborides.

Shick[13] calculated θ_R and θ_X for a number of borides by means of the modified Lindemann relations:

$$\theta_R = K_L(T_C/M_R)^{1/2}\, V_R^{-1/3} \text{ and } \theta_X = K_L(T_C/M_X)^{1/2}\, V_X^{-1/3}, \qquad (6)$$

where T_C is the melting point, and K_L, the Lindemann constant, is 137 when V_R and V_X are taken as the molar volumes of pure metal and nonmetal in cm^3/mole. Schick's θ_R values are lower and θ_X values higher than Kaufman's, and Schick's S°_{298} and $C_{p,298}$ values are in general agreement with experimental data for the borides listed in Table 2, but for CrB_2 and MoB_2 (not in table) Schick's method gives S°_{298} values that are about 8 J/mole-K too high.

Thus, although substantial progress has been made in methods for estimating C_ℓ, each of the existing procedures has deficiencies. Examination

Table 2 Debye temperatures of the metal (θ_R) and nonmetal (θ_X) constituents of various compounds, and a comparison with θ_R°, the Debye temperature of the elemental metal.

Compound	θ_R, K[a]	θ_R°, K[b]	θ_R/θ_R°	θ_X, K[a]
TiB_2	620, 498	362	1.71, 1.38	1302, 1422
ZrB_2	440, 342	254	1.73, 1.35	1277, 1479
HfB_2	320, 251	206	1.55, 1.22	1299, 1503
VB_2	- , 489	408	- , 1.20	- , 1328
NbB_2	425, 370	286	1.49, 1.29	1245, 1481
TaB_2	320, 270	229	1.40, 1.18	1309, 1514
VC	475	408	1.16	1400
Cr_3C_2	500	492	1.02	1000
VN	375	408	0.92	1100
ZrN	400	254	1.57	900
Al_2O_3	750	390	1.92	1100
Ga_2O_3	360	253	1.42	1075
HfO_2	275	206	1.33	850
ThO_2	250	148	1.69	775
MgF_2	375	323	1.16	750
CaF_2	375	232	1.62	550
ZnF_2	250	230	1.09	620
		Ave.	1.38	

a)The first entries of θ_R and θ_X for the diborides are from Kaufman,[17] and the second from Schick.[13] Entries of θ_R and θ_X for the remaining compounds are from Hoffman et al.[1]
b)θ_R° is calculated from low-temperature heat capacity data.[18]

of the data in Table 2 suggests a simpler and more effective approach. We find that θ_R shows little change with the type of refractory compound. For example, θ_R values of 251 and 320 K for HfB_2 are comparable to 275 K for HfO_2. Furthermore, θ_R correlates well with θ_R°, the Debye temperature for the pure metal. The ratio θ_R/θ_R° for the cases considered averages 1.38 with a maximum deviation of ±35%. θ_X values appear to remain relatively constant within a given class of compound, and to decrease in a regular manner as one goes from borides to fluorides. On the basis of the above arguments, C_ℓ is evaluated from Debye functions by estimating θ_R and θ_X as follows. θ_R is taken to be 1.38 times θ_R°. θ_X is taken to be 1375 K for borides, 1230 K for carbides, 1090 K for nitrides, and 950 K for oxides. The Debye metal and nonmetal contributions are apportioned according to their atomic fractions in each compound.

ANHARMONIC LATTICE VIBRATIONS

Anharmonicities in the lattice vibrations lead to a heat capacity term

$$C_a = AC_{\ell}T, \qquad (7)$$

where A is a parametric constant that represents departure of the shape of the potential energy curve from a harmonic oscillator. Since β is also a function of anharmonicity, we expect a direct correlation between A and β, and therefore A should be roughly in inverse proportion to ΔE_a. C_a represents a relatively small contribution to C_p, and is difficult to separate out from the other contributions to C_p when analyzing experimental data. Gopal[19] indicates on theoretical grounds that C_a should not exceed 10% of the heat capacity of vacancy contributions. Hence, C_a should reach a value of less than about 3% of C_p near the melting point. A values of 6.0×10^{-5} K^{-1} for Na at 200 K,[20] and 6.2×10^{-5} K^{-1} for Ge at ~270 K,[21] have been derived from experimental data. Based on these limited observations, it is concluded that $A = 12\ \Delta E_a^{-1}$, where ΔE_a is in J/g-atom, and that C_a is uncertain by a factor of 2.

CONDUCTION ELECTRONS

The contribution of conduction electrons to C_p is given by

$$C_e = \gamma_e T, \qquad (8)$$

where γ_e depends on the density of energy states of conduction electrons at the Fermi level. Normally, γ_e is a characteristic constant for a given substance, but in a few special cases may show a temperature dependence if the Fermi level is near a peak in the density of energy states. We will assume for our purposes that γ_e is invarient with temperature.

Examination of γ_e data on the electrically conductive borides[17,22-28] and carbides,[29,30] indicates that γ_e is generally of the same order as in the pure metals,[18] provided that γ_e is taken on the basis of 1 g-atom of metal atoms in the compounds. More specifically, Th and U compounds have γ_e values that are equal to that in the free metals, while most other compounds have γ_e values of about 1/3 that in the free metals. We will therefore accept these as our estimation basis, and also assume that the nitrides will behave similarly to the carbides and borides. C_e will be assumed to be zero for all of the oxides and the other non-electrically-conductive compounds. Our estimates of γ_e may be uncertain by a factor of 2.

f ELECTRON ENERGY STATES

For lanthanides and actinides and their compounds, the 4f and 5f electrons are well screened so that the crystal field interaction is weak. Consequently, these substances have energy states at levels comparable to those in the free ions. Contributions of the f electron energy states, C_f, are designated as Schottky anomalies, and if the energy states are known, may be calculated from the expression[31]

$$C_f = \frac{1}{RT^2}\left\{\frac{\sum_i E_i^2\, g_i\, \exp(-E_i/RT)}{\sum_i g_i\, \exp(-E_i/RT)} - \left[\frac{\sum_i E_i\, g_i\, \exp(-E_i/RT)}{\sum_i g_i\, \exp(-E_i/RT)}\right]^2\right\}, \quad (9)$$

where g_i represents the multiplicity (2J + 1) for each energy state E_i. Sufficient data are available on crystal spectra to obtain the excited states in +3 lanthanides[31,32] and +3 and +4 actinides,[33,34] to calculated C_f. A difficulty remains in assigning the exact energy levels of the degenerate ground states, since these low-lying levels contribute significantly to C_f at room temperature and below.

From the available data[32] on degenerate levels in the ground state of the +3 lanthanides, Ce^{+3} is found to have 3 doublets at levels of about 0, 150, and 400 cm^{-1}; Sm^{+3}, 3 doublets at 0, 80, and 200 cm^{-1}; Eu^{+3} and Lu^{+3}, no degeneracies; Gd^{+3}, negligible splitting of ground state levels; and the remaining lanthanides have a distribution of states ranging from 0 to about 650 cm^{-1}. For the actinides, the ground state splitting for the +3 states[35,36] is similar to the corresponding lanthanides, but for the +4 states[35,37] is considerably greater and ranges up to about 3000 cm^{-1}. Using these observations as guidelines, the distribution of energy states can be estimated with sufficient accuracy to account for the contribution of C_e over the entire temperature range.

SPIN-ORDER MAGNETIC STATES

Magnetic spin-order states can occur in elements or compounds of the 3d transition series, the lanthanides, and the actinides. Transitions of magnetic spin-order states characteristically show a lambda-shaped heat capacity curve that results from a cooperative order-disorder transformation. The ordered state may be ferromagnetic, antiferromagnetic, or ferimagnetic, and the disordered state is paramagnetic. For the 3d transition series, magnetic transitions may occur above or below room temperature, and make a major contribution to C_p. Because of large uncertainties involved in predicting the existence and magnitude of magnetic transitions in the 3d series, we need to rely on actual measurements rather than attempt to make predictions.

In the lanthanide and actinide series, magnetic transitions generally occur below room temperature and have a relatively small effect on C_p since a relatively small number of energy states are involved.[38] Because of the smallness of the effect, it is adequate for our purposes to treat the magnetic transition as a Schottky anomaly, and to assume that is properly accounted for as part of the C_f calculation.

LATTICE DEFECTS

Defect concentrations in equilibrium with the lattice are given by

$$N_d = \exp(\Delta S_d/R)\exp(-\Delta E_d/RT), \quad (10)$$

where N_d is the ratio of defects to lattice sites, and ΔS_d and ΔE_D are the entropy and energy of defect formation, respectively. Assuming ΔS_d and ΔE_d to be independent of temperature and taking the derivative, $d(N_d \cdot \Delta E_d)/dT$, gives

$$C_d = (\Delta E_d^2/RT^2)\exp(\Delta S_d/R)\exp(-\Delta E_d)RT). \quad (11)$$

The problem reduces to determining values of ΔS_d and ΔE_d.

In the case of pure metals, experimentation has established[39,41] that Schottky vacancies are of dominant importance (concentration of ~1%) as the melting point is approached. Examination of C_p data on metals shows that both ΔE_d and ΔS_d correlate with atomization energy, i.e.,

$$\Delta E_d = 0.32\ \Delta E_a,\ \text{J/g-atom}, \quad (12)$$

$$\Delta S_d = 23.0 + 2.0 \times 10^{-5}\ \Delta E_a,\ \text{J/g-atom-K}. \quad (13)$$

For compounds, a variety of defects occur, such as Schottky or Frenkel disorder, impurity effects, and nonstoichiometric compositions. Taking a strictly empirical approach and ignoring the specifics of the defects, there is evidence that the activation energy for diffusion (ΔE_{diff}) correlates with ΔE_a,[42] i.e.,

$$\Delta E_{diff} = 0.6\ \Delta E_a, \quad (14)$$

which holds well for cation diffusion and approximately for anion diffusion. If one now assumes that $\Delta E_d = 0.55\ \Delta E_{diff}$ (true for vacancy formation in metals[39]), then $\Delta E_d = 0.33\ \Delta E_a$, which agrees with Equa. (12). On the basis of these observations, it is concluded that Equas. (12) and (13) apply not only to metals but also to compounds, and C_d is evaluated from Equa. (11).

RESULTS AND DISCUSSION

Using the same general methods outlined here, the author earlier calculated C_p values for all of the borides.[43] In Table 3, a comparison is given between calculated and experimental values of S_{298} and C_p for borides. Agreement between experiment and calculation is excellent, especially for C_p. Unfortunately, the experimental data do not extend up to a sufficiently high temperature to check the calculated defect contributions, C_d. Within the range covered however, it is apparent that the calculated C_p values agree with experiment to within about ±3% from room temperature on up. This is comparable to the experimental uncertainties in much of the work. We anticipate that similar agreement will be obtained in future comparisons for carbides, nitrides, and oxides.

Table 3 Calculated and experimental S°_{298} and C_p values for borides.[43]

Boride	S°_{298}, J/g-atom-K		C_p, J/g-atom-K, at various temperatures					
			298 K		1000 K		2000 K	
	Calc.	Exper.	Calc.	Exper.	Calc.	Exper.	Calc.	Exper.
LaB_6	11.42	11.88	14.52	13.85	25.65	25.19	-	-
NdB_6	13.97	14.77	14.64	14.14	26.82	27.03	-	-
B_4C	5.19	5.44	10.25	10.63	22.47	22.84	26.74	28.03
TiB_2	10.25	9.50	15.23	14.77	24.94	25.10	28.41	29.62
ZrB_2	12.76	11.97	15.90	16.07	24.81	24.06	27.70	27.45
HfB_2	14.39	14.27	16.19	16.57	24.85	26.82	-	-
NbB_2	12.05	12.76	15.90	16.02	25.44	27.36	-	-
TaB_2	13.68	13.72	16.15	15.98	25.15	25.61	-	-
UB_2	20.79	18.49	18.33	18.58	28.03	29.71	-	-

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